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Review

Erbium ions oscillator strength and emission enhancement in antimony phosphate amorphous matrix

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ABSTRACT

For the first time we report the Er^{3+} ions concentration dependent physical, absorption and emission properties of melt quench synthesized antimony glass having composition $(60 - x)Sb_2O_3$–$35P_2O_5$–$5MgO$–xEr_2O_3 ($0.1 \le x \le 0.9$ mol.%). Transparent glass samples having light yellow and deep pink colors are obtained. Glass density varied between 4.4 and 4.46 g/cm^3 as the Er_2O_3 contents are increased. Glass with 0.3 mol.% of Er_2O_3 revealed the highest density, lowest band gap energy, and maximum refractive index. UV–Vis–NIR spectra exhibited ten absorption bands accompanied by peak shift. Bonding of Er^{3+} ions with ligands is found to alter from covalent to ionic character. Oscillator strength followed the trend of $^2H_{11/2} > {}^4G_{11/2}$, $^4G_{9/2} > {}^4F_{9/2} > {}^4I_{13/2} > {}^4F_{7/2} > {}^4I_{11/2} > {}^4F_{5/2}$, $^4F_{3/2} > {}^4I_{9/2} > {}^4S_{3/2}$. Room temperature emission spectra under 380 nm excitations comprised of intense (centered at 481.5, 457.5, 444, 438, 431, 421, and 410.5 nm) and weak (centered at 746.5, 538, 528.5, and 506 nm) peaks. Emission peaks revealed intensity enhancement with increasing concentration of Er_2O_3. The enhancement in oscillator strength for $^4G_{11/2}$, $^4G_{9/2}$ states absorption, the high intensity of emission band in the blue region and large refractive index (2.28) makes these glasses prospective for down-conversion solid state violet and blue lasers as well as other photonic devices.

Contents

1. Introduction

Recently, rare earth (RE) ions doped glasses emerged as very important photonic materials due to several merits than crystalline competitors. The advantages in terms of different sizes, shapes, simple methods of preparation and high transparency made glasses as suitable host materials for lasing action [1,2]. The up-conversion and down-conversion luminescence processes are widely investigated in the rare earth element especially for trivalent ions. Among all RE, Er^{3+} is the most active candidate. A RE solubility as much as 10 mol.% is achieved with different low phonon glass host [3–16]. The emission intensity of RE ions depends greatly on the glass host and their characteristics. They decide the strength of multi-phonon decay, the nature of metastable energy levels population (storage), rate of cross relaxation, energy transfer and the concentration of rare earth active ion [6]. In addition, incorporation of various glass formers for the host can enhance the up-conversion efficiency via the reduction of multi-phonon relaxation mediated non-radiative loss [17–18]. The rate of multi-phonon decay relates to the vibrational energy stretching. For instance, the energy up-conversion for silicate glasses (1060–1150 cm^{-1}), germinate glasses (800–975 cm^{-1}), tellurite glasses (600–850 cm^{-1}), fluoride glasses (500–600 cm^{-1}) and chalcogenide glasses (200–300 cm^{-1}) are demanding for solid state lasers [9,17].

Antimony glasses is a promising host material with special characteristic such as high thermal stability with glass transition temperature of 300 °C, linear refractive index of ≈2, transmittance window from 380 to 2000 nm and low phonon energy (605 cm^{-1}) of Sb–O–Sb bond

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[19–22]. Antimony oxide can exist in three forms including Sb_2O_3, Sb_2O_5, or combination of the two oxidation states (Sb_2O_4) [23]. Sb_2O_5 is preferred to be use with tri valance cation oxide which has tetrahedral coordination. It cannot make glass on its own due to the supply of required oxygen to the structure stabilization [24]. The antimony based glasses possess major limitations including weak field strength of Sb^{+3} that make it favorable for crystallization and high volatilization rate [25,26]. The ability of antimony oxide to form glass can be enhanced in the binary or ternary glass phase [24,27]. One of the most striking features of antimony trioxide or antimony orthophosphates ($SbPO_4$) is associated to the existence of lone electronic pairs in one of the polyhedra corners. Consequently, it offers an opportunity to acquire different phase formations with unusual electrical and optical properties [28].

Conversely, phosphate glass formers are advantages over borate or silicate glasses due to its ease of preparation, large thermal expansion coefficient, high refractive index and electrical conductivity, low melting temperature, and low transformation temperature. Furthermore, wide range of structural arrangements in three dimension including chains, rings or branching (ultra-, meta-, pyro-, and orthophosphate) allow to manipulate their physical and chemical properties. They possess great accommodation ability of active ions concentration without changing their interesting properties [29–30]. However, their low chemical durability limits them from widespread application. To overcome this limitation and to improve the chemical durability, many oxides (Sb_2O_3, Bi_2O_3, SiO_2, MnO_2, etc) are incorporated into the phosphate glass but at the expense of stability [31–34]. The main actions of alkaline earth metals (called modifier) such as MgO in the glass network structure are to break the bridging oxygen (BO) bonds and create non-bridging oxygen (NBO). This lowers the melting temperature by acting as ionic cross-links between the NBOs of two individual chains if the modifier cations are divalent or have higher valances. In addition, they supply oxygen and enhance the cationic coordination in the glass network [24]. Despite gamut research activities in RE doped glassy materials, the RE doped antimony is rarely explored. It may be due to the mild toxicity of antimony or complex phase formation as well as instability of underlying microstructure.

The present work attempts to explore the possibility of synthesizing thermally stable Er^{3+} doped antimony glass. The influence of varying Er^{3+} concentration on the physical and optical properties of these glasses is determined.

2. Experimental

Glasses of chemical composition $(60 - x)$ Sb_2O_3–$35P_2O_5$–5MgO–xEr_2O_3 (where $0.1 \le x \le 0.9$ mol.%) are prepared using melt-quenching method. High purity analytical grade oxides of Sb_2O_3, P_2O_5, MgO and Er_2O_3 are weighted and thoroughly grounded. The mixture in the powder form is melted in a high purity platinum crucible at 1350 °C in air for 3 h. Upon achieving the desired viscosity, the molten glass mixture is casted into a steel mold and annealed at 250 °C for 2 h. Samples are finally cut and polished to appropriate dimensions for further characterizations at room temperature. Glass composition and their codes are enlisted in Table 1.

Bruker D8 Advance X-ray diffractometer (XRD) is used to verify the amorphous nature of prepared samples with Cu–Kα radiations ($\lambda = 1.54$ Å) operated at 40 kV and 100 mA. The structure and elemental composition of samples are analyzed by employing EIGMA™ (Zeiss Supra 35 v) field emission scanning electron microscope (FESEM) attached with EDX, which operated at accelerating voltages of 5–30 kV. Samples are coated with Au to make them conductive prior to qualitative analysis. Absorption spectra in the wavelength range of 400–1650 nm are recorded via Perkin-Elmer UV–VIS–NIR Lamda 900 spectrometer equipped with a deuterium lamp and halogen lamp with a resolution of 1 nm. Room temperature emission spectra in wavelength range of 200 to 800 nm are recorded using Perkin Elmer LS-55 luminescence spectrometer with pulsed Xenon lamp as a illuminating source of excitation (380 nm).

The weight and atomic percent for each element present in the glass are estimated via,

$$weight\,\%\ of\ atom(i) = N_i N_o M_i / \sum_i N_i N_o M_i \tag{1}$$

$$atomic\,\%\ of\ atom(i) = N_i N_o / \sum_i N_i N_o \tag{2}$$

where N_i, N_o and M_i represent the atom concentration, number of atom and atomic mass respectively of the atom i and $i = 1, 2, 3$ and 4.

Glass density (ρ) is measured using Archimedes principle with toluene as immersion liquid. The density is calculated using.

$$\rho = \left[\frac{W_a}{W_a - W_L} \times (\rho_\circ - d)\right] + d. \tag{3}$$

The molar volume (V_m) yields,

$$V_m = \frac{M_w}{\rho} \tag{4}$$

where W_a weight in the air, W_L weight in the immersion liquid, $\rho_\circ$ is the density of toluene, d density of air and M_w is molecular mass.

Erbium ion concentration, mean inter-ionic distance (r_i) and the polaron radius was calculated via the relations [35,36]:

$$N\left(\frac{ions}{cm^3}\right) = \frac{\rho \times N_{avo} \times n_i x_i}{M_w}. \tag{5}$$

$$r_i(\text{Å}) = \left(\frac{1}{N}\right)^{1/3}. \tag{6}$$

$$r_p = \frac{1}{2}\left(\frac{\pi}{6N}\right)^{1/3}. \tag{7}$$

Following Shelby [37], the field strength (F) was calculated via:

$$F(cm^{-2}) = \left(\frac{Z}{r_p^2}\right) \tag{8}$$

Table 1
Glass compositions and Er_2O_3 concentration dependent variation in physical parameters including density (ρ), molecular weight (M_w), molar volume (V_m), Er^{3+} ion number concentration (N), interionic distance, ri (Å) and polaron radius, rp (Å) and F, field strength (cm^{-2}).

Glass codes	Mol.%				ρ (g/cm^3) ± 0.01	M_w (gm/mol) ± 0.01	V_m (cm^3/mol) ± 0.01	(N) × 10^{19} (ion/cm^3) ± 0.01	ri (Å) ± 0.01	rp (Å) ± 0.01	F × 10^{14} ± 0.01
	Sb_2O_3	P_2O_5	MgO	Er_2O_3							
SPME0.0	60.0	35	5.0	0.0	4.43	226.6	51.15	–	–	–	–
SPME0.1	59.9	35	5.0	0.1	4.44	226.6	51.05	2.35	34.86	14.05	1.51
SPME0.2	59.7	35	5.0	0.3	4.46	226.6	50.86	7.10	24.14	9.73	3.16
SPME0.3	59.5	35	5.0	0.5	4.43	226.6	51.251	11.74	20.41	8.22	4.43
SPME0.4	59.3	35	5.0	0.7	4.4	226.6	51.64	.16.32	18.29	7.37	5.51
SPME0.5	59.1	35	5.0	0.9	4.41	226.6	51.57	21.01	16.81	6.77	6.52